

PATENT SPECIFICATION

(11) 1 546 809

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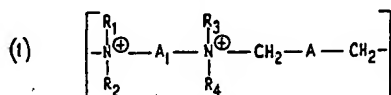
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(54) POLYMERIC QUATERNARY AMMONIUM SALTS,
 PROCESS FOR THEIR MANUFACTURE AND THEIR USE

(71) We, CIBA-GEIGY AG, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

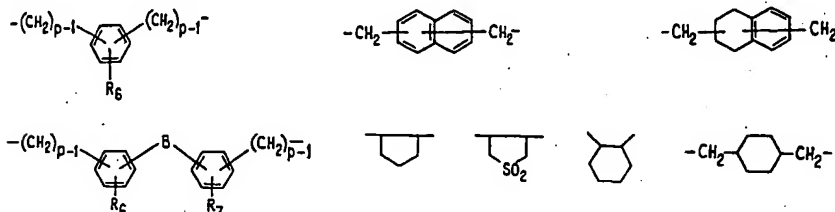
The present invention relates to polymeric quaternary ammonium salts in which the cationic units correspond to the formula

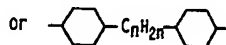


in which R_1 , R_2 , R_3 and R_4 are identical or different from one another and denote optionally substituted alkyl, cycloalkyl or alkenyl with at most 20 carbon atoms, aryl or aralkyl, or R_1 and R_2 and/or R_3 and R_4 , together with the nitrogen atom to which they are bonded, form an optionally substituted heterocyclic ring with 3 to 6 ring members, A_1 is $-(CH_2)_m-$, in which m is a number from 1 to 20, which is optionally interrupted by at least one $-S-$,

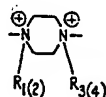


or $-CH=CH-$ grouping or substituted by at least one halogen atom, hydroxyl, nitrile, alkyl, hydroxyalkyl, alkoxy, carboxyl or carbalkoxy radical or at least one optionally substituted aryl or aralkyl radical; a deoxypolyoxyalkylene radical of formula $-(alk-O)_x-alk$, "alk" representing an alkylene group and x being at least 1, or a radical of the formulae

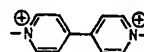




or, together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formula



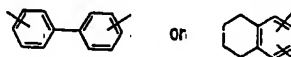
or



5 wherein R_1 and R_3 are identical or different from one another and are hydrogen; alkyl, hydroxyalkyl or halogenoalkyl each with 1 to 4 carbon atoms; hydroxyl, halogen, carbonyl, carbalkoxy or phenyl; B is a direct bond, $-\text{O}-$, 5



10 $-\text{S}-$, $-\text{SO}_2-$ or optionally substituted alkylene, n is a number from 1 to 6, p is a number from 1 to 3, preferably 1 or 2 and A_2 is a radical of the formula 10



or



15 The radicals R_1 , R_2 , R_3 and R_4 in the cationic units of the polymeric quaternary ammonium salts of the formula (1) can be straight-chain or branched alkyl radicals with 1 to 20 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert.-butyl, hexyl, octyl, isooctyl, tert.-octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl or eicosyl. 15

Alkyl radicals with 1 to 10, and especially with 1 to 4, carbon atoms are preferred; methyl and ethyl are particularly suitable.

20 Substituted alkyl radicals are, for example, hydroxyalkyl, cyanoalkyl, alkoxyalkyl, alkylthioalkyl, alkylcarbonylalkyl, alkylsulphonylalkyl, arylcarbonylalkyl and arylsulphonylalkyl, in which aryl is a mononuclear, binuclear or trinuclear aromatic hydrocarbon, especially phenyl or naphthyl; alkylcarboxylic acid, carbalkoxyalkyl and dicarbalkoxyalkyl; and carboxamidoalkyl, which is optionally N- or N,N-substituted by lower alkyl (C_1-C_4) or aryl, for example phenyl. 20

25 The cycloalkyl radicals are preferably cyclopentyl and cyclohexyl, which can optionally be substituted. 25

30 The alkenyl radicals can contain 2 to 20 carbon atoms. Those with 2 to 10, or, in particular, with 2 to 4, carbon atoms are preferred. Suitable alkenyl radicals are those which correspond to the alkyl radicals mentioned. The substituents mentioned for the alkyl radicals can generally also be used for the alkenyl radicals. 30

35 Aryl and aralkyl radicals are, in particular, phenyl and benzyl, which may optionally be substituted by hydroxyl, cyano, halogen (fluorine, chlorine, bromine or iodine) or carboxyl; alkyl, hydroxyalkyl, cyanoalkyl, alkoxy and alkylthio, in which lower alkyl and alkoxy radicals are preferred; alkoxyalkyl, carbalkoxyalkyl and dicarbalkoxyalkyl, in which there are preferably in each case 1 to 4 carbon atoms in the alkyl part and the alkoxy part; alkylcarboxylic acid, in which alkyl preferably contains 1 to 4 carbon atoms; or carboxamidoalkyl, which is optionally N- or N,N-substituted by lower alkyl (C_1-C_4). 35

40 The two substituents on each nitrogen can also form, together with the nitrogen atom to which they are bonded, an optionally substituted heterocyclic ring with 5 or 6 ring members. Examples of such heterocyclic rings are the piperidine morpholine, thiomorpholine, pyrrolidine or imidazoline ring. 40

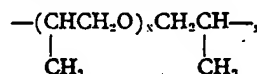
45 The bridge member A_1 is, for example, an alkylene grouping of the formula $-(\text{CH}_2)_m-$, in which m is an integer from 1 to 20 and preferably 1 to 12. The alkylene grouping can be interrupted by a sulphur atom or by 45



or $-\text{CH}=\text{CH}-$; several of these groups are optionally present. Possible substituents, which are bonded to the alkylene chain, can be hydroxyl, halogen, especially fluorine, chlorine and bromine, nitrile; alkyl, hydroxyalkyl or alkoxy each with preferably 1 to 4 carbon atoms, for example, methyl, ethyl, propyl, isopropyl and butyl, hydroxymethyl or hydroxyethyl or methoxy, ethoxy, propoxy and butoxy, and also carboxyl ($-\text{COOH}$) and carbalkoxy, in which the alkoxy radical can contain 1 to 20 carbon atoms.

Other possible substituents of the alkylene chain are aryl and aralkyl, preferably phenyl and benzyl, which are optionally further substituted by e.g. lower alkyl, halogen or hydroxyl.

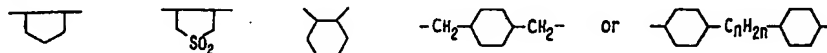
If the bridge member A_1 is a deoxypolyoxyalkylene radical of formula $-(\text{alk}-\text{O})_x-\text{alk}-$, "alk" representing an alkylene group and x being at least 1, preferred such radicals are reoxypolyoxyethylene radicals and in particular, deoxypolyoxypropylene radicals: $-(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2-$ or



in which x is at least 1. The usual upper limit for x can be taken as 50. Preferred values for x are between 1 and 40 and most preferably between 4 and 40.

A_1 can also be an aromatic bridge member which is derived from above-defined mononuclear or binuclear aromatic compounds (benzene or naphthalene). Examples are optionally substituted phenylene, which is optionally linked to the nitrogen atoms via methylene groupings ($-\text{CH}_2-$); unsubstituted naphthalene and tetrahydronaphthalene linked to the nitrogen atoms via methylene groupings; optionally substituted diphenyl, diphenyl oxide, diphenyl sulphide, diphenylsulphone or benzophenone. Possible substituents on these aromatic bridge members are lower alkyl, lower hydroxyalkyl or lower halogenoalkyl each with 1 to 4 carbon atoms, hydroxyl, halogen, especially chlorine and bromine, carboxyl, carbalkoxy and phenyl.

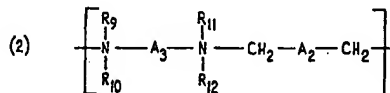
Other bridge members containing cyclic groupings are, in particular, groupings of the formula



in which n is an integer from 1 to 6.

Bridging between the two nitrogen atoms can also be effected via the substituents (R_1-R_4), which are bonded to the nitrogen atoms. Including the two nitrogen atoms, this then gives, for example, piperazine, 1,4-diazabicyclo-(2,2,2)-octane or dipyrilidyl groupings.

Particularly suitable polymeric quaternary ammonium salts contain the cationic units of the formula

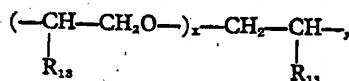


in which R_9 , R_{10} , R_{11} and R_{12} are identical or different from one another and are alkenyl with 2 to 20 carbon atoms, cycloalkyl with 5 or 6 carbon atoms; alkyl, hydroxyalkyl, cyanoalkyl, alkoxyalkyl, alkylthioalkyl or alkylcarbonylalkyl each with up to 10 carbon atoms; arylcarbonylalkyl, alkylsulphonylalkyl or arylsulphonylalkyl each with 1 to 4 carbon atoms in the alkyl part; alkylcarboxylic acid with 1 to 4 carbon atoms in the alkyl part; carbalkoxyalkyl or di-(carbalkoxy)-alkyl each with 1 to 4 carbon atoms in the alkoxy part and with 1 to 4 carbon atoms in the alkyl part; carboxamidoalkyl which has 1 to 10 carbon atoms in the alkyl part and is optionally N-substituted by alkyl with 1 to 4 carbon atoms or aryl; or are phenyl or benzyl, optionally substituted by hydroxyl, cyano, halogen or carboxyl, by alkyl, hydroxyalkyl, cyanoalkyl, alkoxy or alkylthio each with up to 4 carbon atoms, by alkoxyalkyl, carbalkoxyalkyl or di-(carbalkoxy)-alkyl each with 1 to 4 carbon atoms in the alkyl part and with 1 to 4 carbon atoms in the alkoxy part, by alkylcarboxylic acid with 1 to 4 carbon atoms in the alkyl part, or by carboxamidoalkyl which has 1 to 4 carbon atoms in the alkyl part and is itself optionally N-substituted by with 1 to 4 carbon atoms alkyl; or R_9 and R_{10} and/or R_{11} and R_{12} , together with the nitrogen atom to which they are bonded, form an option-

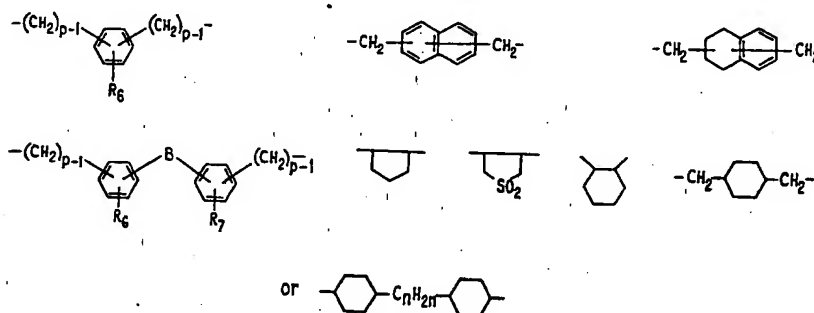
ally substituted heterocyclic ring with 5 or 6 ring members, A_3 is $-(CH_2)_m-$, in which m is a number from 1 to 20, which is optionally interrupted by at least one $-S-$,



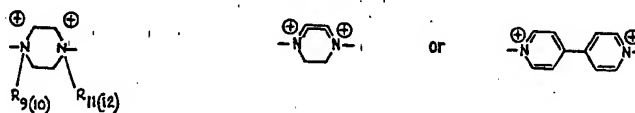
5 or $-\text{CH}=\text{CH}-$ grouping or substituted by at least one chlorine atom, hydroxyl, or nitrile radical, alkyl, alkoxy or hydroxyalkyl radical each with 1 to 4 carbon atoms, carboxyl radical, carbalkoxy radical with 1 to 20, and preferably 1 to 4, carbon atoms in the alkoxy part or by an optionally substituted phenyl or benzyl radical;



10 or a radical of the formula

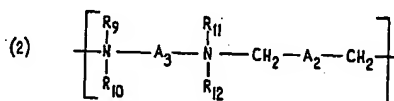


15 or, together with the nitrogen atoms and at least one of the substituents which are bonded to each of the nitrogen atoms, is a radical of the formulae

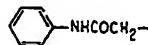


R_{13} is hydrogen or methyl and x is at least 1 and R_6 , R_7 , B , A_2 , n and p have the previously indicated meanings.

20 Further preferred salts are, in particular, those polymeric quaternary ammonium salts in which the cationic units correspond to the formula



25 in which R_{13} , R_{10} , R_{11} and R_{12} are identical or different from one another and are alkyl, hydroxyalkyl, alkoxyalkyl, alkylthioalkyl or cyanoalkyl with up to 4 carbon atoms; cyclopentyl, cyclohexyl, alkenyl with 2 to 4 carbon atoms, $\text{CH}_3\text{COCH}_2\text{---}$, $\text{HOOC---CH}_2\text{---}$, $\text{CH}_3\text{OOCCH}_2\text{---}$, $\text{H}_2\text{C}_2\text{OOCCH}_2\text{---}$, $(\text{CH}_3\text{OOC})_2\text{CH---}$, $\text{H}_2\text{NCOCH}_2\text{---}$ or

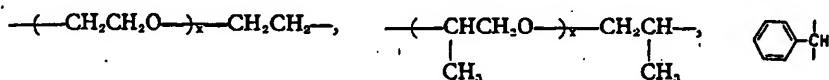
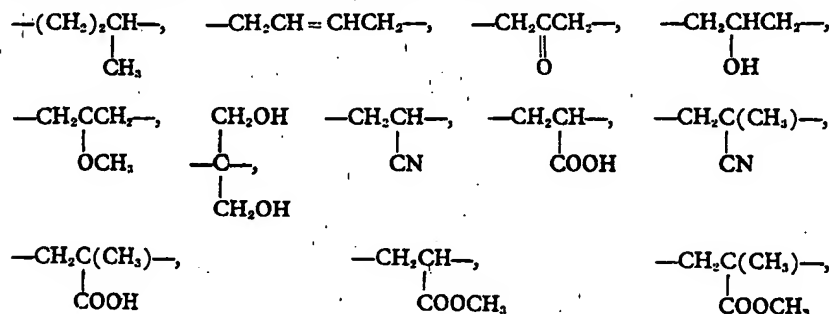


30 or are phenyl or benzyl, optionally substituted by hydroxyl, amino, cyano, fluorine, chlorine or bromine, by alkyl, hydroxyalkyl, alkoxy or alkylthio, each with 1 or 2 carbon atoms, by cyanomethyl, by alkoxyalkyl, carbalkoxyalkyl or di-(carboxyalkyl), each with 1 or 2 carbon atoms in the alkyl part and 1 or 2 carbon atoms in the alkoxy part, by $-\text{CH}_2\text{COOH}$, $-(\text{CH}_2)_2\text{COOH}$ or by carboxamidoalkyl which has 1 or 2 carbon

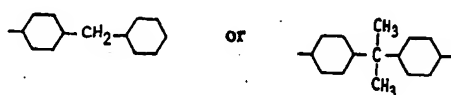
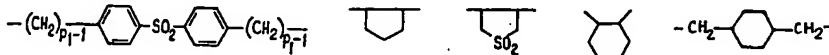
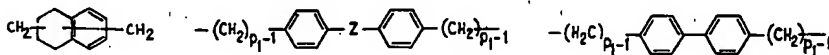
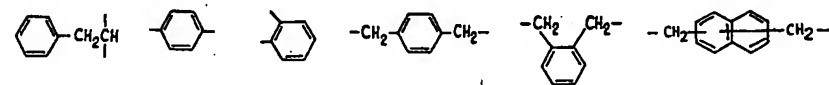
atoms in the alkyl part and is itself optionally N-substituted by lower alkyl; or R_{15} and R_{16} and/or R_{17} and R_{18} , together with the nitrogen atom to which they are bonded, form a heterocyclic ring of the formula



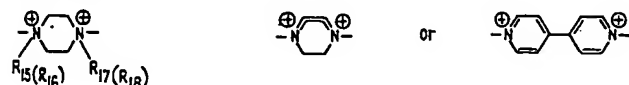
5 and A_1 is $-(CH_2)_m-$, in which m , is a number from 1 to 12,



10



15 in which x is at least 1, $-Z-$ is $-O-$ or $-S-$, and p_1 is 1 or 2, or together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formula



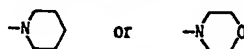
20 Particularly advantageous compounds of the formula (3) are those in which R_{15} , R_{16} , R_{17} , and R_{18} are identical or different from one another and denote alkyl or hydroxyalkyl with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, CH_3OOCCH_2- , $C_2H_5OOCCH_2-$ or benzyl, or R_{15} and R_{16} and/or R_{17} and R_{18} , together with the nitrogen atom to which they are bonded, form a heterocyclic ring of the formula

5

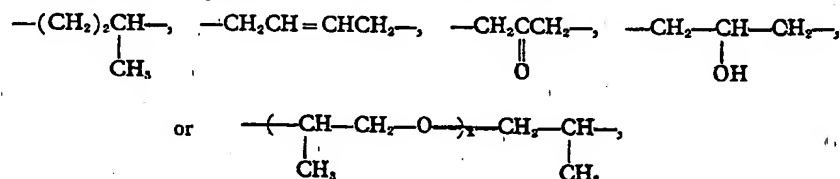
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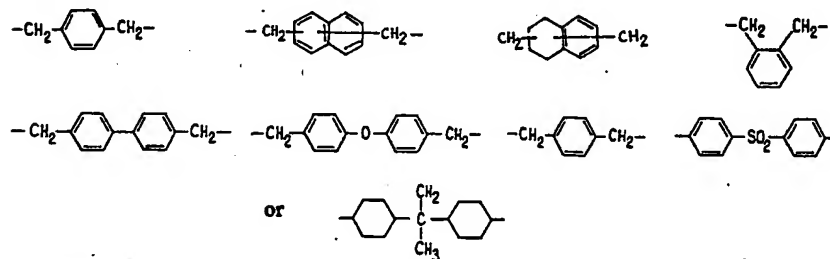
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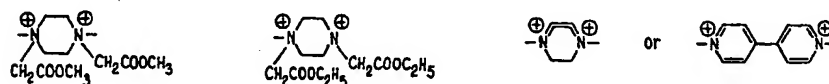
and A_4 is $\text{---}(\text{CH}_2)_m\text{---}$, in which m , is a number from 1 to 12,



5 in which x is at least 1,

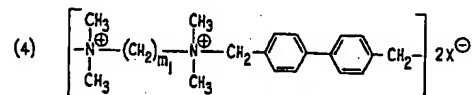


10 or, together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formulae

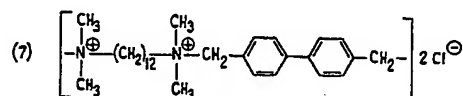
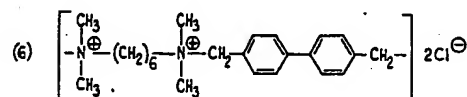
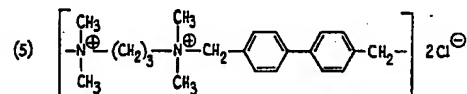


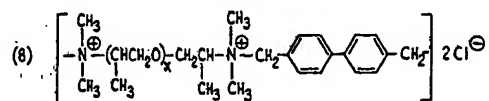
15 In the case of the cationic units of the formula (2), and also in the formulae which follow, these units can also be isomers or mixtures of isomers since the diphenyl or the tetrahydronaphthalene radical can be substituted by the methylene ($\text{---CH}_2\text{---}$) groups in different positions. To avoid listing all of the isomers each time, for the diphenyl radical only the p,p'-substituted isomer is given in each case.

Polymeric quaternary ammonium salts with recurring units of the formulae which follow may, for example, be mentioned individually:

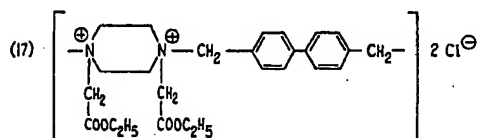
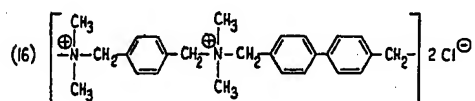
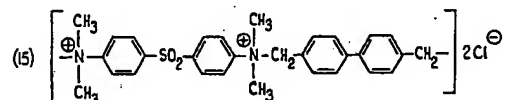
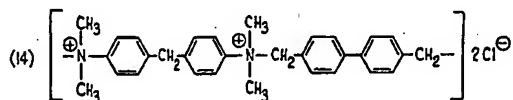
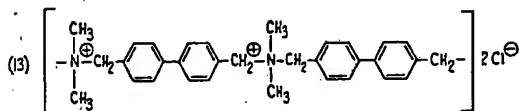
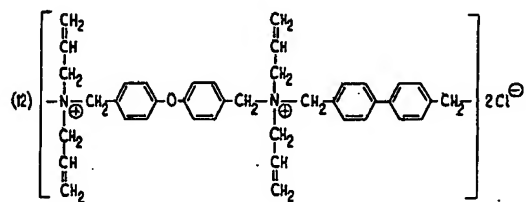
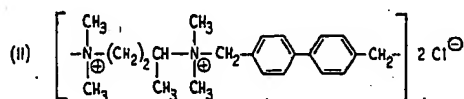
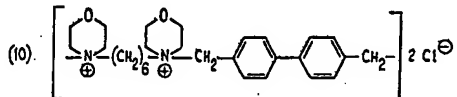
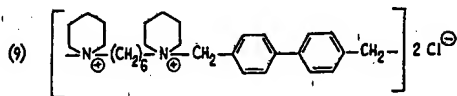


20 in which m_1 is 1 to 12 and X is halogen.

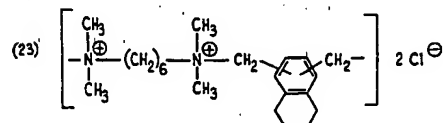
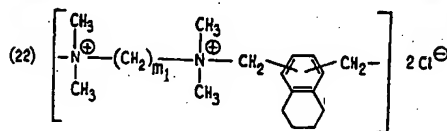
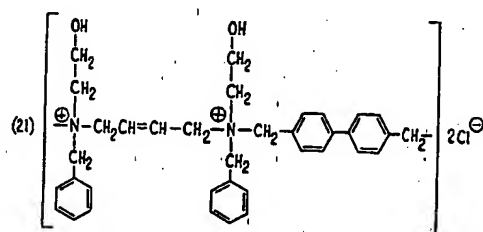
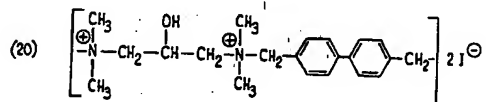
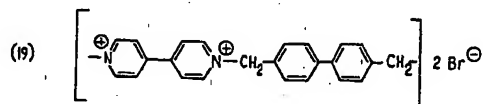
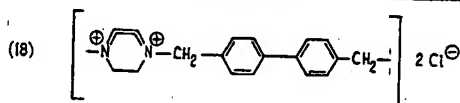




in which x is at least 1;



The compound of the formula (17) is preferably manufactured by reacting piperazine with 4,4'-(bis-chloromethyl)-diphenyl and subsequently quaternising the reaction product with ethyl chloroacetate.

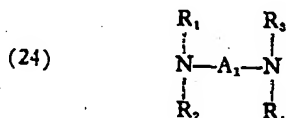


Suitable anions for the polymeric quaternary ammonium salts according to the invention are all of the customary inorganic or organic anions which do not form sparingly soluble complexes with the cations, since the ammonium salts should preferably be water-soluble. Examples which may be mentioned are the anions of the mineral acids or of low-molecular organic acids. Suitable anions are, for example, the halogen anions, e.g. I^{\ominus} , Br^{\ominus} and especially Cl^{\ominus} , or methyl-sulphate ($\text{CH}_3\text{SO}_4^{\ominus}$), ethyl-sulphate ($\text{C}_2\text{H}_5\text{SO}_4^{\ominus}$) and toluenesulphonate or nitrate or sulphate.

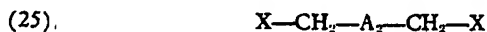
The polymeric quaternary ammonium salts according to the invention can have molecular weights of e.g. 400 or 500 up to 50,000 and preferably up to 25,000, and in particular from 1,500 to 20,000.

The ammonium salts can be manufactured according to known methods by, for example, reacting diamines with corresponding dihalogeno compounds in molar ratios of about 1:2 to 2:1, and preferably in equimolar amounts.

Thus, the compounds of the formula (1) can be obtained by reacting diamines of the formula

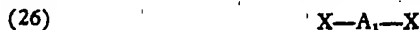


in which R_1 , R_2 , R_3 and R_4 as well as A_1 have the previously indicated meanings, with dihalides of the formula

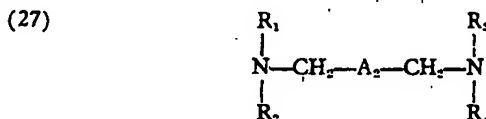


in which X is halogen and A_2 has the previously indicated meaning.

A further possibility can be to react dihalides of the formula



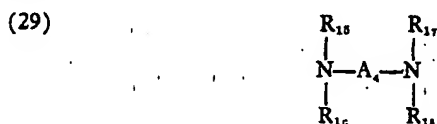
in which A_1 and X have the previously indicated meanings, with diamines of the formula



in which R_1 , R_2 , R_3 , R_4 and A_2 have the previously indicated meanings. For example, diamines of the formula



in which R_9 , R_{10} , R_{11} , R_{12} and A_3 have the previously indicated meanings, can be employed for the particularly suitable ammonium salts of the formula (2), whilst



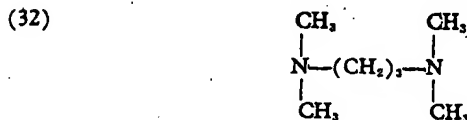
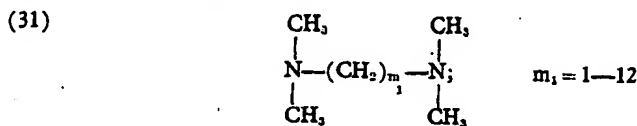
in which R_{15} , R_{16} , R_{17} and R_{18} as well as A_4 have the previously indicated meanings, are employed for the preferred ammonium salts of the formula (3). In this case, a dichloro compound of the formula



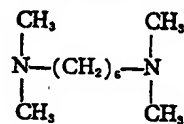
is employed as the dihalogeno compound. Isomers, or mixtures of isomers, of compounds of the formula (28) can optionally be employed.

The compounds of the formulae (2) and (3) can also be manufactured using starting compounds which are analogous to the compounds of the formulae (26) (dihalides) and (27) (diamines).

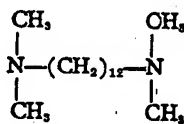
The following diamines



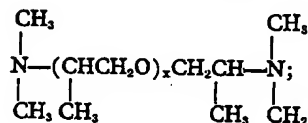
(33)



(34)



(35)

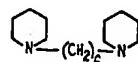


x is at least 1

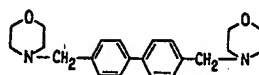
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and

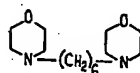
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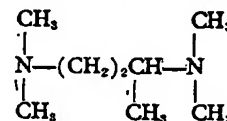
(37a)



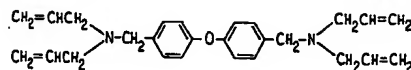
(37b)



(37c)

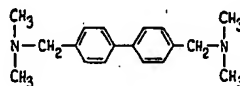


(38)



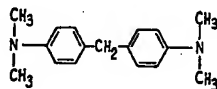
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(39)

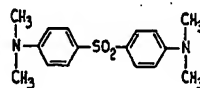


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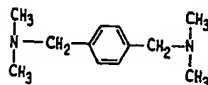
(40)



(41)



(42)



(43)



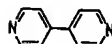
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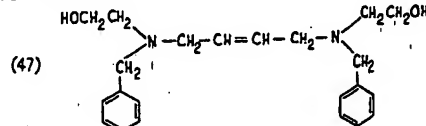
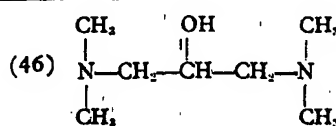
(44)



15

(45)





can be employed for the manufacture of the reaction products and the recurring units of the formulae (4) to (23).

The starting compounds (diamines and dihalides) for the manufacture of the polymeric quaternary ammonium salts according to the invention are generally known compounds which are readily accessible by chemical synthesis.

4,4'-Bis-(chloromethyl)diphenyl can be obtained by chloromethylation of diphenyl. The diamines can be manufactured, for example, by reacting the corresponding α,ω -dihalogeno compounds with secondary amines, such as dimethylamine, piperidine, diallylamine or hydroxyethylbenzylamine, or by a N,N,N',N'-permethylation of a primary diamine according to known methods, preferably by reaction with formaldehyde and formic acid (Leuckart reaction). The diamines of the formula (35) are manufactured from polypropylene glycols by reaction with 2 mols of propyleneimine.

The manufacture of the ammonium salts according to the invention can be carried out in solvents which are inert with respect to the reactants, for example alcohols, glycols or ketones, for example, acetone, or cyclic ethers, e.g. dioxane or tetrahydrofuran. Amongst the alcohols, the lower alcohols, especially methanol, are preferred. The reaction temperature usually depends on the boiling points of the solvents employed and can be room temperature (20°C) or elevated temperature, for example 20 to 150°C, preferably 50 to 100°C.

The reaction can optionally also be carried out in water or water/alcohol mixtures as the solvent or, in certain cases, also without a solvent.

Due to the preferred use of cheap and readily accessible dichloro compounds in the manufacture of the polymeric quaternary ammonium salts according to the invention, the salts preferably contain chlorine ions as anions. The introduction of other anions can, preferably, be so carried out that other anions are introduced into the ammonium salts containing chlorine ions (the reaction products) by, for example, ion exchange.

As a rule, the polymeric quaternary ammonium salts according to the invention are usually prepared in the form of mixtures and not as pure compounds. The indicated molecular weights can, therefore, be regarded only as average molecular weights.

The polymeric quaternary ammonium salts according to the invention can be employed in neutral, acid or alkaline dyebaths. They are suitable as dyeing auxiliaries, especially as levelling agents, in processes for dyeing and printing textile materials made of natural or synthetic fibres.

Textile materials made of natural fibres which can be used are those made of cellulosic materials, especially of cotton, and also of wool and silk, whilst the textile materials made of synthetic fibres are, for example, those made of high-molecular polyesters, for example polyethylene terephthalate or polycyclohexanedimethylene terephthalate; polyamides, e.g. those of hexamethylenediamine adipate, poly- ϵ -caprolactam or ω -aminoundecanoic acid; polyolefines or polyacrylonitriles, and also of polyurethanes, polyvinyl chlorides and polyvinyl acetates, as well as of cellulose 2½-acetate and cellulose triacetate. The synthetic fibres mentioned can also be employed as mixtures with one another or as a mixture with natural fibres, e.g. cellulose fibres or wool. These fibre materials can be in all stages of processing which are suitable for a continuous procedure, for example, in the form of cable, tops, filaments, yarns, woven fabrics, knitted fabrics or nonwoven articles.

Dyeing formulations can be in the form of aqueous or aqueous-organic solutions or the polymeric quaternary ammonium salts according to the invention, yet further addidispersions or in the form of printing pastes which contain, in addition to a dyestuff and the polymeric quaternary ammonium salts according to the invention, yet further additives, for example, acids, salts, ureas and further auxiliaries, e.g. oxyalkylation products of fatty amines, fatty alcohols, alkylphenols, fatty acids and fatty acid amides.

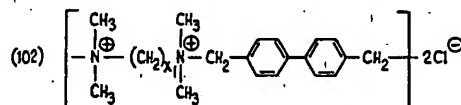
The polymeric quaternary ammonium salts are particularly suitable as retarders when dyeing polyacrylonitrile fibre materials with cationic dyestuffs and in some cases also when dyeing anionically modified polyester fibre materials.

The cationic dyestuffs which are used can belong to very diverse groups. Examples of suitable dyestuffs are diphenylmethane dyestuffs, triphenylmethane dyestuffs, rhodamine dyestuffs and azo or anthraquinone dyestuffs containing onium groups and also thiazine, oxazine, methine and azomethine dyestuffs.

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c) In a third batch with the same reactants (molar ratio of diamine to dihalide 2:1), a reaction product which has a viscosity $\eta = 0.10$ (25°C, methanol, [dl/g]) and an average molecular weight of 1,500 is obtained.

Analogous reactions of 4,4'-bis-(chloromethyl)-diphenyl with N,N,N',N'-tetramethyl-substituted ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,10-diaminodecane give, again in quantitative yield, reaction products containing recurring units of the general formula



The values for x_1 , the viscosity and the average molecular weight are given in Table I which follows.

TABLE I

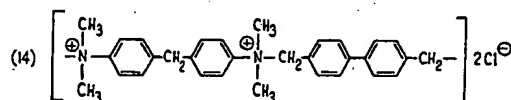
Example	x_1	η 25°C, methanol [dl/g]	average molecular weight
1 d	2	0.09	1,300
1 e	3	0.40	5,900
1 f	4	1.26	19,000
1 g	6	1.35	19,800
1 h	8	0.44	6,500
1 i	10	0.46	6,600

Example 2.

12.7 g (0.05 mol) of N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane and 11.5 g (0.045 mol) of 4,4'-bis-(chloromethyl)-diphenyl in 100 ml of methanol are heated to the reflux temperature for 24 hours.

The solvent is then distilled off, the residue is taken up in 150 ml of ether and the solution is stirred and then filtered and the product is dried in vacuo at 40°C. A powder which dissolves in water to give a clear solution is obtained.

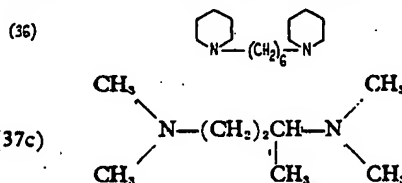
Yield: 23.7 g (98% of theory) of a reaction product containing recurring units of the formula



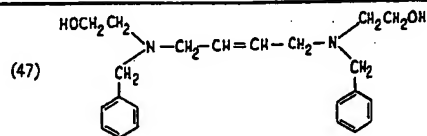
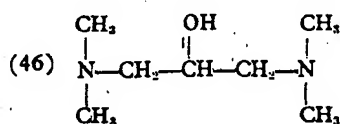
Viscosity η : 0.13 (25°C, methanol [dl/g])
Average molecular weight: 1,900

Example 3.

The procedure is as described in Example 1 and equimolar amounts of 4,4'-bis-(chloromethyl)-diphenyl and diamines of the following formulae:



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can be employed for the manufacture of the reaction products and the recurring units of the formulae (4) to (23).

The starting compounds (diamines and dihalides) for the manufacture of the polymeric quaternary ammonium salts according to the invention are generally known compounds which are readily accessible by chemical synthesis.

4,4'-Bis-(chloromethyl)diphenyl can be obtained by chloromethylation of diphenyl. The diamines can be manufactured, for example, by reacting the corresponding α,ω -dihalogeno compounds with secondary amines, such as dimethylamine, piperidine, diallylamine or hydroxyethylbenzylamine, or by a $\text{N},\text{N},\text{N}',\text{N}'$ -permethylation of a primary diamine according to known methods, preferably by reaction with formaldehyde and formic acid (Leuckart reaction). The diamines of the formula (35) are manufactured from polypropylene glycols by reaction with 2 mols of propyleneimine.

The manufacture of the ammonium salts according to the invention can be carried out in solvents which are inert with respect to the reactants, for example alcohols, glycols or ketones, for example, acetone, or cyclic ethers, e.g. dioxane or tetrahydrofuran. Amongst the alcohols, the lower alcohols, especially methanol, are preferred. The reaction temperature usually depends on the boiling points of the solvents employed and can be room temperature (20°C) or elevated temperature, for example 20 to 150°C , preferably 50 to 100°C .

The reaction can optionally also be carried out in water or water/alcohol mixtures as the solvent or, in certain cases, also without a solvent.

Due to the preferred use of cheap and readily accessible dichloro compounds in the manufacture of the polymeric quaternary ammonium salts according to the invention, the salts preferably contain chlorine ions as anions. The introduction of other anions can, preferably, be so carried out that other anions are introduced into the ammonium salts containing chlorine ions (the reaction products) by, for example, ion exchange.

As a rule, the polymeric quaternary ammonium salts according to the invention are usually prepared in the form of mixtures and not as pure compounds. The indicated molecular weights can, therefore, be regarded only as average molecular weights.

The polymeric quaternary ammonium salts according to the invention can be employed in neutral, acid or alkaline dyebaths. They are suitable as dyeing auxiliaries, especially as levelling agents, in processes for dyeing and printing textile materials made of natural or synthetic fibres.

Textile materials made of natural fibres which can be used are those made of cellulosic materials, especially of cotton, and also of wool and silk, whilst the textile materials made of synthetic fibres are, for example, those made of high-molecular polyesters, for example polyethylene terephthalate or polycyclohexanedimethylene terephthalate; polyamides, e.g. those of hexamethylenediamine adipate, poly- ϵ -caprolactam or ω -aminoundecanoic acid; polyolefines or polyacrylonitriles, and also of polyurethanes, polyvinyl chlorides and polyvinyl acetates, as well as of cellulose 2½-acetate and cellulose triacetate. The synthetic fibres mentioned can also be employed as mixtures with one another or as a mixture with natural fibres, e.g. cellulose fibres or wool. These fibre materials can be in all stages of processing which are suitable for a continuous procedure, for example, in the form of cable, tops, filaments, yarns, woven fabrics, knitted fabrics or nonwoven articles.

Dyeing formulations can be in the form of aqueous or aqueous-organic solutions or the polymeric quaternary ammonium salts according to the invention, yet further addidispersions or in the form of printing pastes which contain, in addition to a dyestuff and the polymeric quaternary ammonium salts according to the invention, yet further additives, for example, acids, salts, ureas and further auxiliaries, e.g. oxyalkylation products of fatty amines, fatty alcohols, alkylphenols, fatty acids and fatty acid amides.

The polymeric quaternary ammonium salts are particularly suitable as retarders when dyeing polyacrylonitrile fibre materials with cationic dyestuffs and in some cases also when dyeing anionically modified polyester fibre materials.

The cationic dyestuffs which are used can belong to very diverse groups. Examples of suitable dyestuffs are diphenylmethane dyestuffs, triphenylmethane dyestuffs, rhodamine dyestuffs and azo or anthraquinone dyestuffs containing onium groups and also thiazine, oxazine, methine and azomethine dyestuffs.

The polyacrylonitrile textile materials can be dyed in the customary manner by introducing the goods to be dyed into an aqueous liquor which has been warmed to about 50 to 60°C and contains the cationic dyestuff, the polymeric quaternary ammonium salt, additives of salts, e.g. sodium acetate and sodium sulphate, as well as acids, e.g. acetic acid or formic acid, then raising the temperature of the dyebath in the course of about 30 minutes to approximately 100°C and then keeping the dyebath at this temperature until it is exhausted. However, it is also possible to add the basic dyestuff only subsequently to the dyebath, for example when the temperature of the bath has risen to about 60°C. Furthermore, it is also possible to pretreat the goods to be dyed, at a temperature of 40 to 100°C, with a liquor which contains the customary salts and acids, as well as the polymeric ammonium salt, but does not yet contain any dyestuff, and only then to add the dyestuff and carry out dyeing at 100°C. Finally, it is also possible directly to introduce the goods to be dyed into the dyebath which has been heated to approximately 100°C and which contains the polymeric ammonium salt.

Those materials which have been manufactured with the additional use of yet further vinyl compounds, for example, vinyl chloride, vinyl acetate, vinylidene chloride, vinylidene cyanide and alkyl acrylates, in addition to acrylonitrile, are also to be understood as polyacrylonitrile fibre materials if the proportion of these other vinyl compounds is not higher than 20%, relative to the weight of the fibre materials.

Appropriate amounts of polymeric quaternary ammonium salts which are employed in these dyeing processes are, in general, in the range of 0.01 to 2 per cent by weight, and especially at 0.05 to 1 or of 0.1 to 1 per cent by weight, relative to the weight of the fibre materials.

The dyeings of polyacrylonitrile fibres produced using the polymeric quaternary ammonium salts as auxiliaries are distinguished by a very high levelness and, at the same time, display a good dyestuff yield on the fibre.

Further applications for the polymeric quaternary ammonium salts according to the invention are: resists when dyeing polyacrylonitrile fibres; dispersing agents, for example for pigments; emulsifiers; cationic fixing agents for improving the fastness to wet processing of cellulosic textile fibre materials or paper dyed with direct dyestuffs and disperse dyestuffs; antistatic agents, especially for textile materials containing synthetic organic fibres; anti-microbial agents; precipitants, for example in the purification of effluents, or flocculating agents, for example for coagulating colloidal aqueous dispersions, for example dyestuff dispersions.

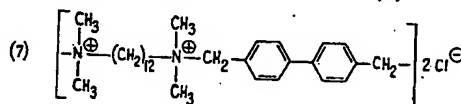
Thus, the polymeric quaternary ammonium salts can be used in particular in processes for dyeing and printing textile materials containing natural or synthetic fibres, for example when dyeing textile materials consisting of polyacrylonitrile fibres; and also in processes for fixing dyestuffs; and also in processes for finishing textile materials, containing synthetic organic fibres, especially for rendering such materials antistatic, or also in processes for purifying effluents, in which case they can be employed as precipitants, and also as flocculating agents in processes for coagulating, for example, colloidal, aqueous dispersions.

In the examples which follow, the parts and the percentages relate to the weight, unless otherwise stated.

Example 1.

a) 109 g (0.435 mol) of 4,4'-bis-(chloromethyl)-diphenyl and 111 g (0.435 mol) of N,N,N',N'-tetramethyl-1,12-diaminododecane in 440 ml of methanol are heated to the reflux temperature for 24 hours.

The solvent is then distilled off and the residue is dried at 40°C. The reaction product dissolves in water to give a clear solution. Yield: 220 g (100% of theory) of a reaction product containing recurring units of the formula (7)



Viscosity: $\eta = 0.54$ (25°C, methanol, [dl/g])

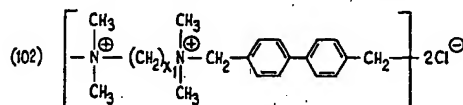
Average molecular weight: 7,900

In this example and the examples which follow, the viscosity is the inherent viscosity. The measured values relate to 0.5% (weight/volume) solutions in methanol. The average molecular weights have been determined from these viscosities.

b) In a second batch with the same reactants, a reaction product which has a viscosity $\eta = 0.52$ (25°C, methanol, [dl/g]) and an average molecular weight of 7,600 is obtained.

c) In a third batch with the same reactants (molar ratio of diamine to dihalide 2:1), a reaction product which has a viscosity $\eta = 0.10$ (25°C, methanol, [dl/g]) and an average molecular weight of 1,500 is obtained.

Analogous reactions of 4,4'-bis-(chloromethyl)-diphenyl with N,N,N',N'-tetramethyl-substituted ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,10-diaminodecane give, again in quantitative yield, reaction products containing recurring units of the general formula



The values for x_1 , the viscosity and the average molecular weight are given in Table I which follows.

TABLE I

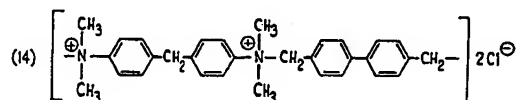
Example	x_1	η 25°C, methanol [dl/g]	average molecular weight
1 d	2	0.09	1,300
1 e	3	0.40	5,900
1 f	4	1.26	19,000
1 g	6	1.35	19,800
1 h	8	0.44	6,500
1 i	10	0.46	6,600

Example 2.

12.7 g (0.05 mol) of N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane and 11.5 g (0.045 mol) of 4,4-bis-(chloromethyl)-diphenyl in 100 ml of methanol are heated to the reflux temperature for 24 hours.

The solvent is then distilled off, the residue is taken up in 150 ml of ether and the solution is stirred and then filtered and the product is dried in vacuo at 40°C. A powder which dissolves in water to give a clear solution is obtained.

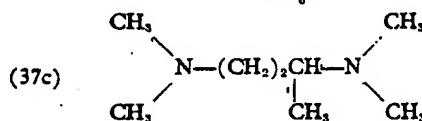
Yield: 23.7 g (98%, of theory) of a reaction product containing recurring units of the formula

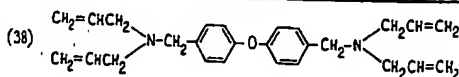


Viscosity η : 0.13 (25°C, methanol [dl/g])
Average molecular weight: 1,900

Example 3.

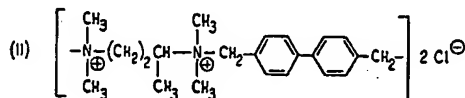
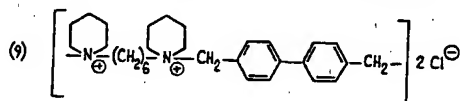
The procedure is as described in Example 1 and equimolar amounts of 4,4'-bis-(chloromethyl)-diphenyl and diamines of the following formulae:



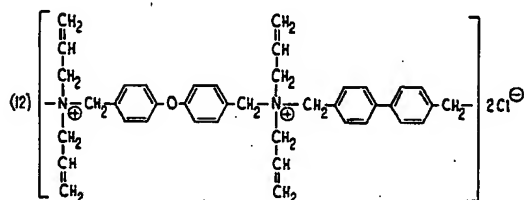


are reacted.

Reaction products containing recurring units of the formulae



and



are obtained in quantitative yield.

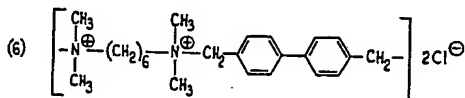
Viscosities: 25°C, methanol [dl/g]

a. $\eta = 0.23$ b. $\eta = 0.19$ c. $\eta = 0.12$

Average molecular weight: a. 3,400 b. 2,800 c. 1,700

Example 4.

a) 86.15 g (0.5 mol) of N,N,N',N'-tetramethyl-1,6-diaminohexane and 125.5 g (0.5 mol) of 4,4'-bis-(chloromethyl)-diphenyl in 300 ml of methanol are heated to the reflux temperature, whilst stirring. A further 200 ml of methanol are introduced into the reaction mixture, which becomes more viscous as the reaction time increases. After 24 hours under reflux, the reaction is ended and the solvent is distilled off. 212 g (100% of theory) of a reaction product containing recurring units of the formula



are obtained. The product dissolves in water to give a clear solution.

Viscosity: $\eta = 1.54$ (25°C, methanol, [dl/g])

Average molecular weight: 23,000

b) 25.12 g (0.1 mol) of 4,4'-bis-(chloromethyl)-diphenyl are dissolved in 80 ml of acetone and the solution is heated to the reflux temperature (56°C). 17.23 g (0.1 mol) of N,N,N',N'-tetramethyl-1,6-diaminohexane, dissolved in 20 ml of acetone, are added in the course of one minute, whilst stirring. An exothermic reaction starts and, at the same time, a colourless precipitate starts to separate out. After 4 hours at the reflux temperature, the reaction is ended and the precipitate is filtered off and dried. 42.3 g (100% of theory) of a reaction product containing the recurring units of the formula (6) are obtained.

The product is a white, hygroscopic powder which dissolves in water to give a clear solution.

Viscosity: $\eta = 0.30$ (25°C, methanol, [dl/g])

Average molecular weight: 4,400.

Example 5.

a) 12.56 g (0.05 mol) of 4,4'-bis-(chloromethyl)-diphenyl and 13 g (0.1 mol) of 1,3-bis-dimethylamino)-propane are heated to 60°C, whilst stirring, for 30 hours.

Example 6.
The procedures are as in Example 4 and equimolar amounts of 4,4'-bis-(chloromethyl)-diphenyl and one of the diamines mentioned below are reacted. Examples 6(a), (b), (c) and (g) follow the procedure of Example 4(a), while Examples 6(d), 5 (e) and (f) follow the procedure of Example 4(b).

TABLE III

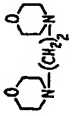

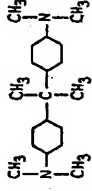


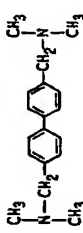
Example	Diamine	Reaction conditions	Yield (% of theory)	Viscosity (η - 25°C [dl/g])	Average molecular weight
(a)		24 hours, methanol, 60°C	25	0.06	900
(b)		27 hours, methanol, 60°C	100	0.04	600
(c)		27 hours, methanol, 60°C	100	0.35	5,100
(d)		4 hours, acetone, 56°C	71	0.05	700 ¹⁾
(e)		4 hours, acetonitrile, 65-70°C	100	-	- ^{1) 2) 3)}

TABLE-III (Continuation)

Example	Diamine	Reaction conditions	Yield (% of theory)	Viscosity (η - 25°C methanol [dl./g])	Average molecular weight
(f)	$(\text{CH}_3\text{CHCH}_2)_2\text{N}(\text{CH}_2)_6\text{N}(\text{CH}_2\text{CHCH}_2)_2\text{OH}$	56 hours, methyl ethyl ketone, 80°C	7	0.08	1,100 ⁴⁾ 5)
(g)		24 hours, methanol, 60°C	100	0.51	7,500

1) The reaction products precipitate during the reaction. After the reaction has ended, they are filtered off and dried.

2) This product was sparingly soluble in water: its chemical structure determined with the aid of elementary analysis and of the infrared spectrum and the nuclear magnetic resonance spectrum.

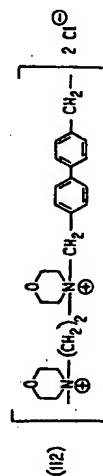
3) 4,4'-Bis-(bromomethyl)-diphenyl was employed.

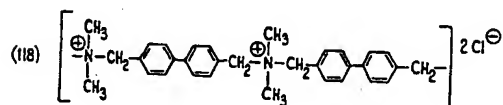
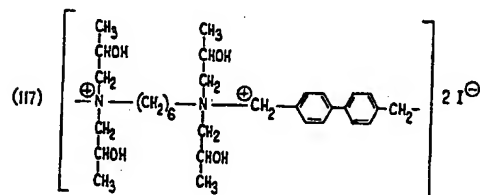
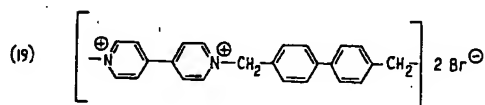
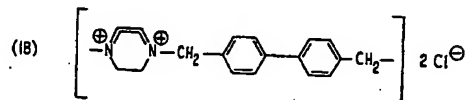
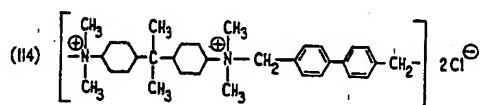
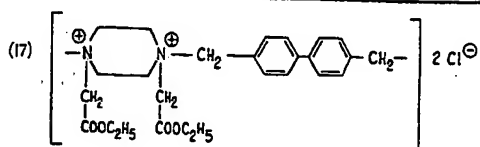
4) The quaternary product was extracted from the reaction mixture with water.

5) 4,4'-Bis-(iodomethyl)-diphenyl was employed.

6) The reaction product is subsequently quaternised with ethyl chloroacetate.

The reaction products of Examples 6a to 6g can be represented by the following structural formulae (recurring units):



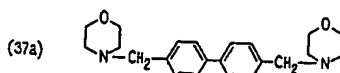


5

5

Example 7.

35.2 g (0.1 mol) of the diamine of the formula

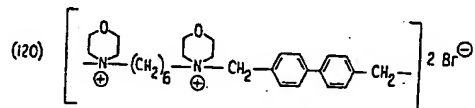


10

and 24.4 g (0.1 mol) of 1,6-dibromohexane in 300 ml of methanol are heated under reflux for 24 hours. The solvent is then distilled off and the residue is taken up in ether in order to remove the constituents which are insoluble in water.

10

A water-soluble reaction product containing recurring units of the formula



15

is obtained.

Yield: 30% of theory.

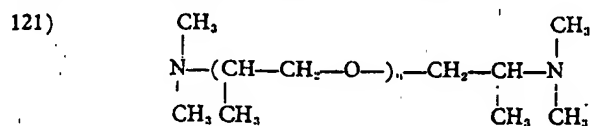
Viscosity: $\eta = 0.06$ (20°C, methanol, [dl/g])

Average molecular weight: 900.

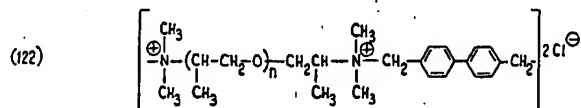
15

Example 8.

Equimolar amounts of a diamine of the formula



5 and 4,4'-bis-(chloromethyl)-diphenyl are reacted in methanol at the reflux temperature for 24 hours. After removing the solvent, reaction products containing recurring units of the formula



are obtained.

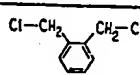
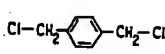
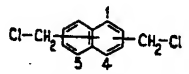
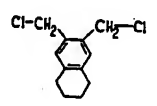
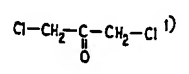
TABLE IV

Example	n	Yield % of theory	Viscosity η	Average molecular weight
a	2.6	100	0.30	4,400
b	5.6	100	0.21	3,100
c	33.1	100	0.68	10,000

Example 9.

10 Equimolar amounts of the dichlorides mentioned in Table V and 4,4'-bis(dimethylaminomethyl)-diphenyl are heated in acetone to the reflux temperature for 24 hours. In the course of the reaction, the reaction product precipitates out. After the reaction has ended, the reaction mixture is cooled and the product which has precipitated is
15 filtered off and dried.

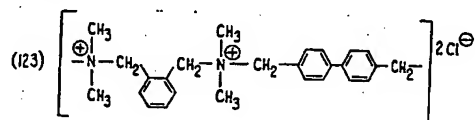
TABLE V

Example	Dichloride	Yield (% of theory)	Viscosity	Average molecular weight
(a)		88.3	0.36	5,300
(b)		94.3	0.29	4,300
(c)	 (ratio of the 1,4:1,5-isomers is 40:60)	100	0.19	2,800
(d)		100	0.22	3,200
(e)		70.5	0.07	1,000

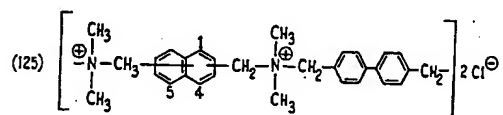
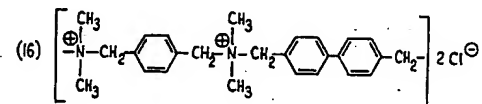
1) Reaction conditions: 24 hours in acetone at room temperature (20 to 25°C).

The reaction products of Examples 9a to 9e can be represented by the following structural formulae (recurring units):

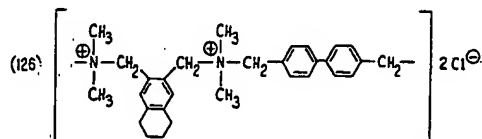
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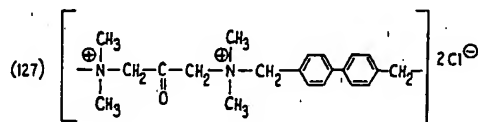
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(1,4:1,5 isomers in a ratio of 40:60)

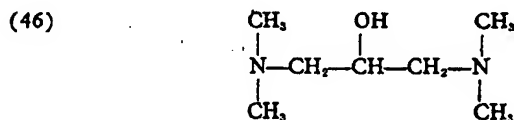


and

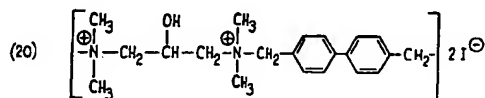


Example 10.

Equimolar amounts of the diamine of the formula



and 4,4'-bis-(chloromethyl)-diphenyl are heated with 1.1 equivalents of sodium iodide in acetone for 48 hours under reflux (56°C). The reaction solution is then filtered. The solvent is distilled off and a colourless reaction product containing recurring units of the formula



is obtained as the residue.

Yield: 72.7% of theory.

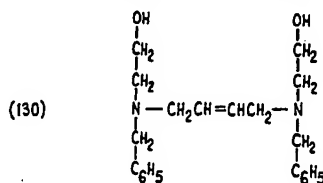
The iodide can be converted into the corresponding chloride by reaction with freshly precipitated silver chloride (24 hours in methanol at 64°C, then filter, remove the solvent and dry the residual product).

Viscosity: $\eta = 0.38$ (25°C, methanol [dl/g])

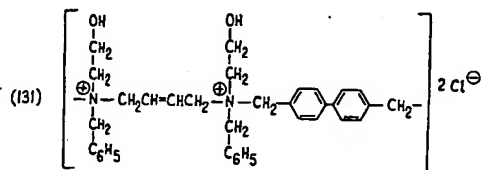
Average molecular weight: 4,100.

Example 11.

Equimolar amounts of the diamine of the formula



and 4,4'-bis-(chloromethyl)-diphenyl are heated in acetone to the reflux temperature (56°C) for 24 hours. After the reaction has ended, the solvent is distilled off and the residue is extracted with hot water. A colourless reaction product containing recurring units of the formula



is obtained from the aqueous solution after removal of the water.

Yield: 47.7% of theory

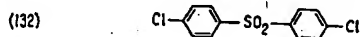
Viscosity: $\eta = 0.1$ (25°C, methanol [dl/g])

Average molecular weight: 1,400.

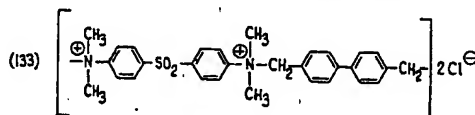
The infra-red spectrum (KBr) shows absorption bands at 3,310, 3,050, 2,960, 2,740, 2,620, 1,970, 1,925, 1,835, 1,660, 1,615, 1,590, 1,505, 1,460, 1,220, 1,090, 1,055, 1,010, 960, 930, 815, 755, 705 and 665 cm^{-1} .

Example 12.

Equimolar amounts of the dichloro compound of the formula



and 4,4'-bis-(dimethylaminomethyl)-diphenyl are reacted as described in Example 9. A reaction product containing recurring units of the formula



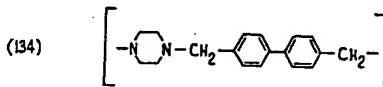
is obtained.

Yield: 23% of theory.

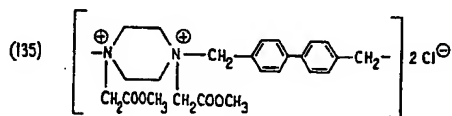
The product is not adequately soluble in methanol, so that it was not possible to determine viscosity values in this solvent. The infra-red spectrum (KBr) displays absorption bands at 3,470, 3,280, 1,615, 1,565, 1,465, 1,375, 1,240, 1,120, 1,075, 1,040, 995, 970, 825, 735, 600, 575, 505, 475 and 420 cm^{-1} .

Example 13.

25.5 g (0.1 mol) of 4,4'-bis-(chloromethyl)-diphenyl and 8.88 g (0.1 mol) of piperazine, together with 11.7 g of sodium carbonate, are taken up in 200 ml of benzene and the mixture is heated to 60°C for 20 hours, whilst stirring. After the reaction has ended, the reaction mixture is cooled to room temperature (20 to 25°C) and filtered and the residue is washed with 400 ml of water and then dried. This gives 14.7 g (55.6% of theory) of a compound containing recurring units of the formula



3.97 g (0.015 mol) of this reaction product are heated with 13.04 g (0.12 mol) of methyl chloroacetate to 80 to 90°C for 15 hours, whilst stirring. After the reaction has ended, the reaction mixture is cooled and the reaction product is extracted with 100 ml of water. After evaporating the aqueous solution, 101 g (14% of theory) of a reaction product containing recurring units of the formula



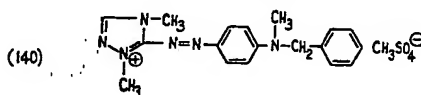
are obtained.

Viscosity: $\eta = 0.17$ (25°C, methanol [dl/g])

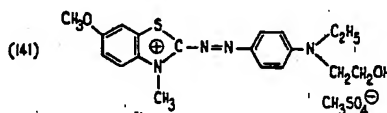
Average molecular weight: 2,500.

Example 14.

50.23 g (0.2 mol) of 4,4'-bis-(chloromethyl)-diphenyl and 26.05 g (0.2 mol) of N,N,N',N'-tetramethyl-1,3-diaminopropane in 200 ml of water are heated to 95°C for 24 hours. The reaction mixture obtained after the reaction has ended and after cooling to room temperature (20 to 25°C) can be further diluted with water, for example with 100 ml, and so employed direct for various applications.



and 0.01 g of the dyestuff of the formula



is then added to the liquor, the temperature being maintained at 98°C.

Dyeing is then carried out for 60 minutes at this temperature, the liquor is cooled slowly to 60°C and the fabric is rinsed and dried.

A slow, constant-shade build-up of the colour shade on the fibre is achieved by the addition of the auxiliary (retarder). The customary cooling after pre-shrinking is no longer necessary.

The resulting grey dyeing is distinguished by outstanding levelness and good penetration and by good fastness to wet processing.

(b) Similar good effects can also be achieved with the reaction products of Examples 1 to 15.

Example 17.

10 g of a fabric made of polyacrylonitrile (Orlon 42 — Du Pont) are introduced, in a dyeing apparatus, into 400 ml of a liquor which contains 0.01 g of an auxiliary according to Example 1(h) and 0.5 g of sodium sulphate and the pH value of which has been adjusted to 4 with 80% strength acetic acid. Whilst agitating continuously, the substrate is treated at 70°C for 10 minutes and 0.15 g of the dyestuff of the formula (139) are then introduced into the liquor. The dye liquor is then warmed to 98°C in the course of 30 minutes and the fabric is dyed for 20 minutes at this temperature. In order to tint the colour shade, 0.01 g of the dyestuff of the formula (141) is added to the dye liquor and dyeing is carried out for a further 30 minutes at 98°C. The dye liquor is then slowly cooled to 60°C and the fabric is rinsed and dried.

A level, brilliant green dyeing with good fastness properties is obtained.

This experiment shows that a dyeing can be "shaded" without further addition of the retarder and without cooling the liquor.

Example 18.

5 g of a fabric made of polyacrylonitrile (Euroacril [Registered Trade Mark] — ANIC) are treated for 10 minutes at 70°C in a dyeing apparatus in 200 ml of a liquor which contains 0.05 g of an auxiliary according to Example 1(g) and the pH value of which has been adjusted to 4 with 80% strength acetic acid. A mixture of dyestuffs consisting of 0.007 g of the dyestuff of the formula (139), 0.006 g of the dyestuff of the formula (140) and 0.01 g of the dyestuff of the formula (141) is then added to the dye liquor and the latter is warmed rapidly to 98°C.

The fabric is then dyed for 60 minutes at this temperature. The liquor is then slowly cooled to 60°C and the fabric is rinsed and dried.

A level grey dyeing with good fastness properties results.

Example 19.

(a) 100 parts of a cotton fabric which has been dyed with 2.5 parts of the dyestuff C.I. No. 29,065, mercerised and bleached are after-treated for 30 minutes at 25°C in 4,000 parts of an aqueous liquor which contains 3 parts of an auxiliary of the formula (102) ($x_1 = 3$, Example 1 e) and the pH value of which has been adjusted to 6 with 80% strength acetic acid.

Compared with a dyeing which has not been after-treated the dyeing after-treated in this way shows a considerable improvement in the water fastness test under severe conditions (SNV Standard 195,819 = DIN 54,006).

(b) The after-treatment (fixing of the dyestuff) can also be carried out with the other reaction products mentioned in Examples 1 to 15 and distinct improvements in the fastness properties of the dyeings are again achieved.

Example 20.

(a) An Orlon fabric (Type 42 — Du Pont) is padded with a liquor which con-

tains, per litre, 15 g of the auxiliary according to Example 1(f), squeezed out to an increase in weight of 110% and dried for 30 minutes at 80°C. The fabric is then set for 30 seconds at 150°C.

The surface resistance of the fabric is measured after drying and after setting. In a second test the measurement is repeated after 5 washes.

The following values were obtained:

TABLE VI

	Surface resistance (Ohms)			
	dried at 80°C		set for 30 seconds at 150°C	
		5 washes		5 washes
untreated	5×10^{13}	1×10^{14}	5×10^{13}	5×10^{13}
treated	5×10^7	9×10^{11}	1×10^9	5×10^{10}

A distinct reduction in the surface resistance is achieved by the described treatment with the auxiliary mentioned; these effects also indicate good fastness to washing. (Permanent antistatic agent).

The soiling characteristics of the fabric are virtually unaffected by the auxiliary applied.

(b) The other reaction products according to Examples 1 to 15 can also be employed analogously and good antistatic effects again result.

Example 21.

(a) An aqueous solution of the reaction product according to Example 1(c) is allowed to run, together with an industrial effluent which contains about 100 ppm of a mixture of reactive dyestuffs and acid dyestuffs, into a settling tank of a sewage-treatment plant. The amount of the reaction product which is introduced into the effluent is 60 ppm. Spontaneous precipitation of the dyestuff takes place. The dyestuff which has precipitated out can be separated off by filtration after only 30 minutes and the residual effluent (the filtrate) can be fed, as completely decolorised effluent, into the sewage system.

As a rule, however, it is not customary to filter; instead, the precipitates are allowed to sediment.

In the present case, the dyestuff which has precipitated settles on the bottom in about 5 to 6 hours and the supernatant water, which is completely decolorised, can be pumped into the sewage system.

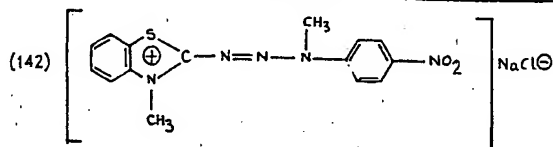
In the case of overdosage of the precipitant no redissolving of the precipitates is observed.

(b) In place of the reaction product according to Example 1 (c), it is also possible, also with good success, to employ the other reaction products mentioned in Examples 1 to 15.

Example 22.

20 g of a fabric made of polyacrylonitrile (Orlon 42 — Du Pont) are treated for 60 minutes at 98°C in a dyeing apparatus in 800 ml of a liquor which contains 0.02 g of the auxiliary according to Example 1(g) and the pH value of which has been adjusted to 4 with acetic acid. The liquor is then cooled and the fabric is rinsed. Subsequently, the fabric pre-treated in this way is dyed, together with an equal amount of a fabric which has not been pre-treated, as follows:

10 g of the pretreated fabric and 10 g of a fabric which has not been pretreated are introduced in a dyeing apparatus, into 800 ml of a liquor which contains 0.03 g of a mixture (1:1) of dyestuffs consisting of the dyestuff of the formula



and Basic Red 22 (C.I. 11,055) and the pH value of which has been adjusted to 4 with acetic acid, and are treated for 60 minutes at 98°C. The liquor is then cooled and the fabric is rinsed, and finished, in the customary manner.

The pre-treated fabric shows a good resist effect and displays only slight (light red) staining, whilst the fabric which has not been pre-treated displays dark red staining. Similar resist effects can also be achieved when the other reaction products of Examples 1 to 15 are used.

Example 23.

(Determination of the bactericidal action)

The destructive effect of the polymeric quaternary ammonium salts is determined in a suspension experiment. Solutions of 1 ppm up to 30 ppm in water are prepared. About 10^5 bacteria per ml of solution are added, as a suspension, to 5 ml of each of the solutions.

The bacteria tested are: 1. *Staphylococcus aureus* SG 511, 2. *Escherichia coli* NCTC 8196 and 3. *Pseudomonas aeruginosa* NCTC 8060.

After specific intervals, a solid nutrient medium, which contains a blocking agent (for example polyoxyethylenesorbitane monooleate) is inoculated with 0.1 ml of the mixture. The number of living bacteria is determined.

The results are given in Tables VII to VIII which follow. The reaction products display a good antibacterial activity towards the three bacteria tested.

Test bacterium: *Staphylococcus aureus* SG 511

TABLE VII

	Concentration of the solutions (ppm)							
	1		3		10		30	
	Bacteria counts per ml. after various times							
Reaction products according to Example	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours
	1.10 ⁵	1.10 ⁴	2.10 ⁴	1.10 ³	1.10 ³	0.3×10 ¹	0	0
	3.10 ⁴	1.10 ³	4.10 ³	3.10 ¹	1.10 ²	0.2×10 ¹	0	0
	1.10 ⁵	1.5×10 ⁴	1.10 ⁴	4.10 ¹	2.10 ²	0.5×10 ¹	3.10 ¹	0
	1.10 ⁵	5.10 ²	1.5×10 ³	5.10 ¹	2.10 ²	0	9.10 ¹	0

Test bacterium: *Escherichia coli* NCTC 8196

TABLE VIII

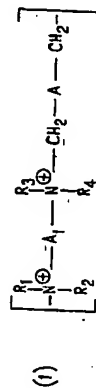
	Concentration of the solutions (ppm)							
	1		3		10		30	
	Bacteria counts per ml. after various times							
	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours
Reaction products according to Example								
1 a)	1.10 ⁵	8.10 ⁴	2.10 ³	1.10 ²	1.5×10 ¹	0	0	0
5 b)	—	—	—	—	1.10 ³	0	0	—
6 d)	—	—	—	—	1.10 ⁴	1.10 ⁴	1.10 ³	0
8 a)	—	—	—	—	3.10 ²	0	5.10 ²	0

Test bacterium: *Pseudomonas aeruginosa* NCTC 8060

Reaction products according to Example	Concentration of the solutions (ppm)									
	1		3		10		30			
	Bacteria counts per ml. after various times									
	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours	1 hour	4 hours
1 a)	1.10 ⁵	8.10 ⁴	1.10 ⁴	15.10 ³	2.10 ³	0.4×10 ¹	0	0	0	0
5 b)	—	—	1.10 ⁴	1.10 ²	3.10 ³	0	2.10 ²	0	0	0
6 d)	—	—	—	—	—	—	1.10 ⁴	0	0	0
8 a)	—	—	—	—	1.10 ⁴	0	2.10 ³	0	0	0

WHAT WE CLAIM IS:—

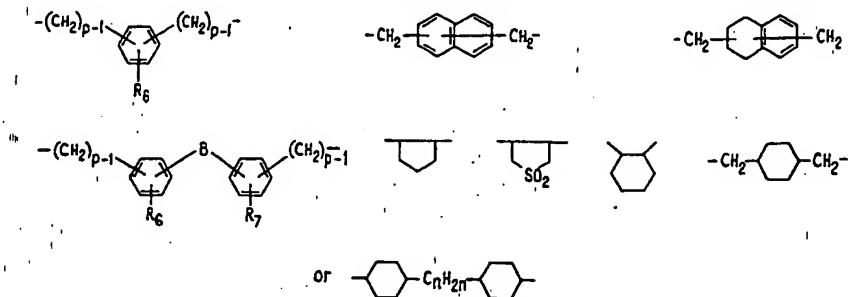
1. A polymeric quaternary ammonium salt in which the cationic units correspond to the formula



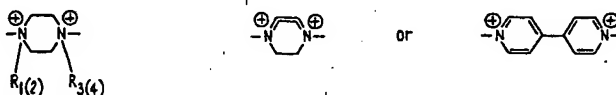
in which R₁, R₂, R₃ and R₄ are identical or different from one another and denote optionally substituted alkyl, cycloalkyl or alkenyl with at most 20 carbon atoms, aryl or alkyl, or R₁ and R₂ and/or R₃ and R₄, together with the nitrogen atom to which they are bonded, form an optionally substituted heterocyclic ring with 3 to 6 ring members, A₁ is —(CH₂)_m—, in which m is a number from 1 to 20, which is optionally interrupted by at least one —S—,



or —CH=CH— grouping or substituted by at least one halogen atom or hydroxyl, nitrile, alkyl, hydroxyalkyl, alkoxy, carboxyl or carbalkoxy radical or by at least one optionally substituted aryl or alkyl radical: a deoxypolyoxyalkylene radical of formula —(alk—O)—alk—, "alk" representing an alkylene group and x being at least 1, or a radical of the formula



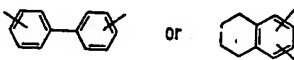
or, together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formula



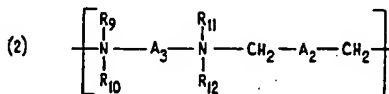
wherein R_6 and R_7 are identical or different from one another and are hydrogen; alkyl, hydroxyalkyl or halogenoalkyl each with 1 to 4 carbon atoms; hydroxyl, halogen, carboxyl, carbalkoxy or phenyl; B is a direct bond, $-\text{O}-$,



$-\text{S}-$, $-\text{SO}_2-$ or optionally substituted alkylene, n is a number from 1 to 6, p is a number from 1 to 3 and A_2 is a radical of the formula



2. A polymeric quaternary ammonium salt according to Claim 1, wherein the cationic units correspond to the formula

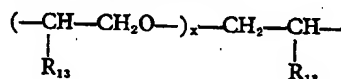


in which R_9 , R_{10} , R_{11} and R_{12} are identical or different from one another and are alkenyl with 2 to 20 carbon atoms, cycloalkyl with 5 or 6 carbon atoms; alkyl, hydroxyalkyl, cyanoalkyl, alkoxyalkyl, alkylthioalkyl or alkylcarbonylalkyl each with up to 10 carbon atoms; arylcarbonylalkyl, alkylsulphonylalkyl or arylsulphonylalkyl each with 1 to 4 carbon atoms in the alkyl part; alkylcarboxylic acid with 1 to 4 carbon atoms in the alkyl part; carbalkoxyalkyl or di-(carbalkoxy)-alkyl each with 1 to 4 carbon atoms in the alkoxy part and with 1 to 4 carbon atoms in the alkyl part; carboxamidoalkyl which has 1 to 10 carbon atoms in the alkyl part and is optionally N-substituted by alkyl with 1 to 4 carbon atoms or aryl; or are phenyl or benzyl, optionally substituted by hydroxyl, cyano, halogen or carboxyl, by alkyl, hydroxyalkyl, cyanoalkyl, alkoxy or alkylthio each with up to 4 carbon atoms, by alkoxyalkyl, carbalkoxyalkyl or di-(carbalkoxy)-alkyl each with 1 to 4 carbon atoms in the alkyl part and with 1 to 4 carbon atoms in the alkoxy part, by alkylcarboxylic acid with 1 to 4 carbon atoms in the alkyl part, or by carboxamidoalkyl which has 1 to 4 carbon atoms in the alkyl part and is itself optionally N-substituted by alkyl with 1 to 4 carbon atoms; or R_9 and R_{10} and/or R_{11} and R_{12} , together with the nitrogen atom to which they are bonded, form an optionally substituted heterocyclic ring with 5 or 6 ring members, A_3 is $-(\text{CH}_2)_m-$, in which m is a number from 1 to 20, which is optionally interrupted by at least one $-\text{S}-$,

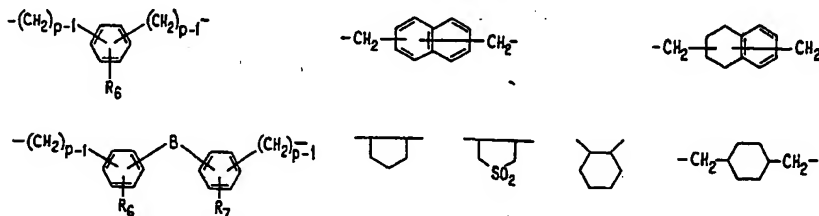


- 5 or —CH=CH— grouping or substituted by at least one chlorine atom, hydroxyl or nitrile radical, alkyl, alkoxy or hydroxyalkyl radical, each with 1 to 4 carbon atoms, carboxyl radical, carbalkoxy radical with 1 to 4 carbon atoms in the alkoxy part or by an optionally substituted phenyl or benzyl radical;

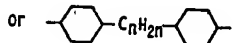
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or a radical of the formulae

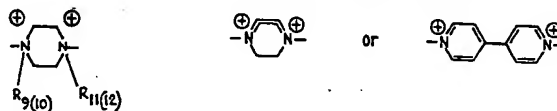


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or, together with the nitrogen atoms and at least one of the substituents which are bonded to each of the nitrogen atoms, is a radical of the formulae

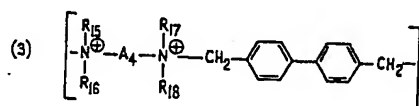


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R₁₃ is hydrogen or methyl and x is at least 1 and R₆, R₇, B, A₂, n and p have the meanings indicated in Claim 1.

3. A polymeric quaternary ammonium salt according to Claim 2, wherein the cationic units correspond to the formula

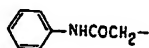
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in which R₁₅, R₁₆, R₁₇ and R₁₈ are identical or different from one another and are alkyl, hydroxyalkyl, alkoxyalkyl, alkylthioalkyl or cyanoalkyl with up to 4 carbon atoms, cyclopentyl, cyclohexyl, alkenyl with 2 to 4 carbon atoms, CH₃COCH₂—, HOOC—CH₂—, CH₃OOCCH₂—, H₅C₂OOCCH₂—, (CH₃OOC)₂CH—, H₂NCOCH₂—,

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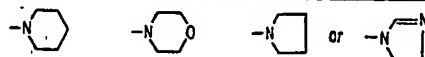
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or phenyl or benzyl, optionally substituted by hydroxyl, cyano, fluorine, chlorine, or bromine, by alkyl, hydroxyalkyl, alkoxy and alkylthio each with 1 or 2 carbon atoms, by cyanomethyl, by alkoxyalkyl, carbalkoxyalkyl and di-(carboxyalkyl), each with 1 or 2 carbon atoms in the alkyl part and 1 or 2 carbon atoms in the alkoxy part, by —CH₂COOH, —(CH₂)₂COOH, or carboxamidoalkyl which has 1 or 2 carbon atoms in the alkyl part and is itself optionally N-substituted by lower alkyl; or R₁₃ and R₁₆, and/or R₁₇ and R₁₈, together with the nitrogen atom to which they are bonded, form a heterocyclic ring of the formulae

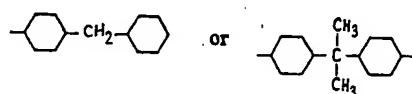
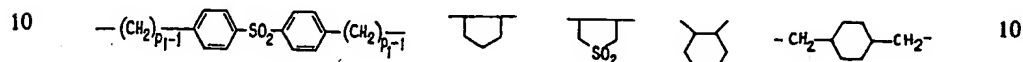
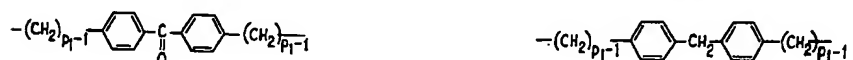
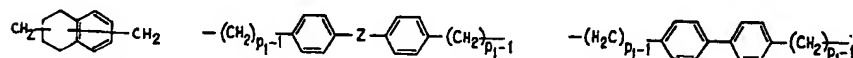
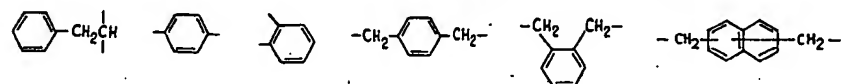
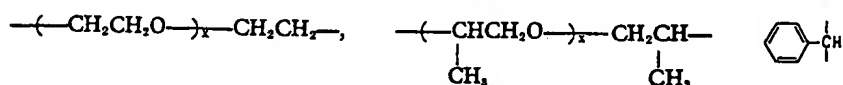
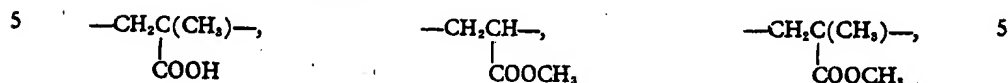
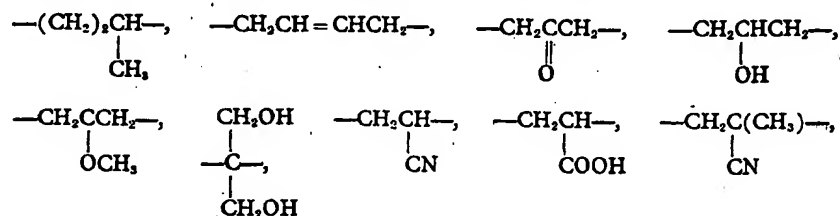
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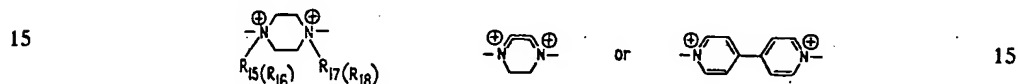
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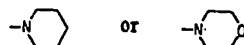
and A_1 is $-(CH_2)_{m_1}-$, in which m_1 is a number from 1 to 12,



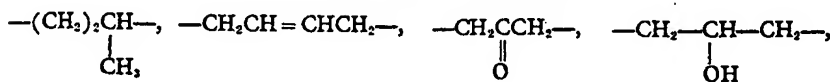
in which x is at least 1, $-Z-$ is $-O-$ or $-S-$, and p_1 is 1 or 2, or together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formulae

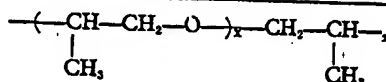


4. A polymeric quaternary ammonium salt according to Claim 3, wherein R_{15} , R_{16} , R_{17} , and R_{18} are identical or different from one another and denote alkyl or hydroxyalkyl each with 1 to 4 carbon atoms, alkenyl with 2 to 4 carbon atoms, CH_3OOCCH_2- , $C_2H_5OOCCH_2-$ or benzyl, or R_{15} and R_{16} and/or R_{17} and R_{18} , together with the nitrogen atom to which they are bonded, form a heterocyclic ring of the formula

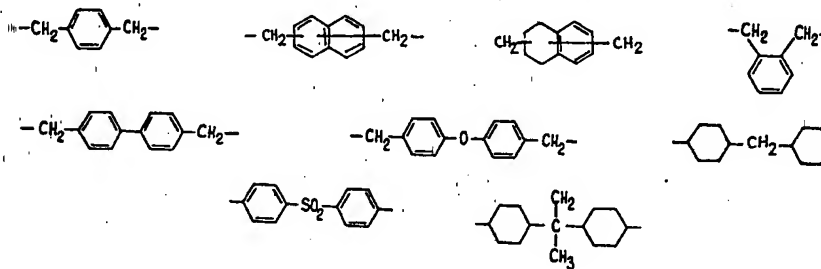


and A_1 is $-(CH_2)_{m_1}-$, in which m_1 is a number from 1 to 12,

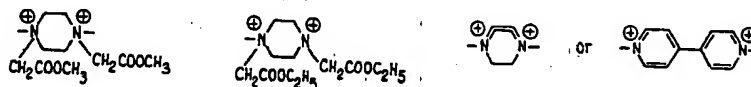




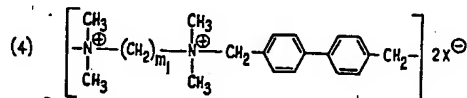
in which at least 1,



or, together with the nitrogen atoms and at least one of the substituents bonded to each nitrogen atom, is a radical of the formulae

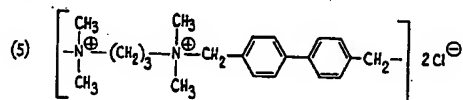


5. A polymeric quaternary ammonium salt according to Claim 3, wherein the recurring units correspond to the formula

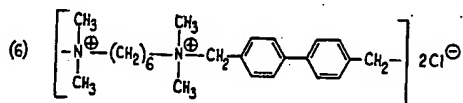


in which m_1 is 1 to 12 and X is halogen.

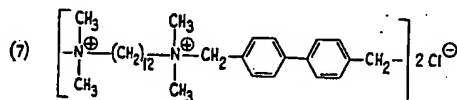
6. A polymeric quaternary ammonium salt according to Claim 5, wherein the recurring units correspond to the formula



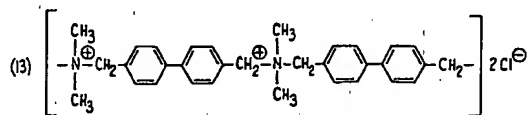
7. A polymeric quaternary ammonium salt according to Claim 5, wherein the recurring units correspond to the formula



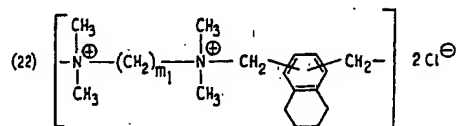
8. A polymeric quaternary ammonium salt according to Claim 5, wherein the recurring units correspond to the formula



9. A polymeric quaternary ammonium salt according to Claim 3, which contains recurring units of the formula

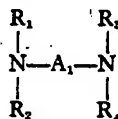


10. A polymeric quaternary ammonium salt according to Claim 2, wherein the recurring units correspond to the formula



5 in which m_1 is 1 to 12.

11. Process for the manufacture of a polymeric quaternary ammonium salt according to Claim 1, wherein a diamine of the formula

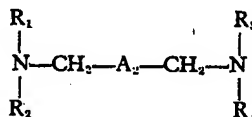


10 in which R_1 , R_2 , R_3 , R_4 and A_1 have the meanings indicated in Claim 1, is reacted with a dihalide of the formula



in which X is halogen and A_2 has the meaning indicated in Claim 1.

12. Process for the manufacture of a polymeric quaternary ammonium salt according to Claim 1, wherein a diamine of the formula

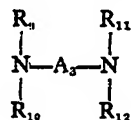


15 in which R_1 , R_2 , R_3 , R_4 and A_2 have the meanings indicated in Claim 1, is reacted with a dihalide of the formula



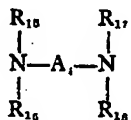
20 in which X is halogen and A_1 has the meaning indicated in Claim 1.

13. Process according to Claim 11, wherein the diamine corresponds to the formula



in which R_9 , R_{10} , R_{11} , R_{12} and A_3 have the meaning indicated in Claim 2.

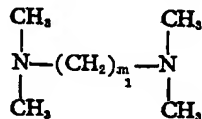
14. Process according to Claim 11, wherein a diamine of the formula



25 in which R_{15} , R_{16} , R_{17} , R_{18} and A_4 have the meanings indicated in Claim 3, is reacted with the dichloride of the formula

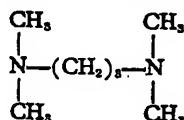


15. Process according to Claim 14, wherein the diamine corresponds to the formula

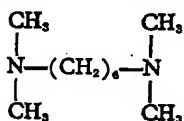


5 in which m_1 is 1 to 12.

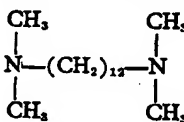
16. Process according to Claim 15, wherein the diamine corresponds to the formula



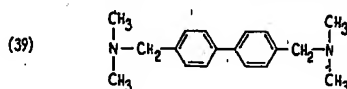
10 17. Process according to Claim 15, wherein the diamine corresponds to the formula



18. Process according to Claim 15, wherein the diamine corresponds to the formula



15 19. Process according to Claim 11 or 12, wherein the diamine corresponds to the formula



20 20. Process according to any one of Claims 11 to 19, wherein the reaction is carried out at room temperature or elevated temperature and in a solvent.

21. Process according to Claim 20, wherein the reaction is carried out at temperatures of 20 to 150°C.

22. Process according to Claim 20, wherein the reaction is carried out in methanol or acetone.

23. Process according to Claim 20, wherein the reaction is carried out in water or water/alcohol mixtures as the solvents.

24. Use of a polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as a dyeing auxiliary.

25. Use according to Claim 24, wherein the quaternary ammonium salt is employed as a levelling agent in dyeing formulations.

26. Use according to Claim 24, wherein the quaternary ammonium salt is employed as a retarder when dyeing polyacrylonitrile fibre materials with cationic dyestuffs or when dyeing anionically modified polyester fibre materials.

27. Use according to Claim 24, wherein the quaternary ammonium salt is employed as a cationic fixing agent for dyeings on textiles and paper.

28. Use of a polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as a dispersing agent and emulsifier.

29. Use of a polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as an antimicrobial agent.

30. Use of a polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as a precipitant or flocculating agent.

31. Use of a polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as an antistatic agent, especially for textile materials containing synthetic organic fibres.
32. Process for dyeing and printing textile materials containing natural or synthetic fibres, wherein the textile materials are dyed with an aqueous or aqueous-organic solution or dispersion, or printed with a printing paste, which contains, in addition to a dyestuff, at least one polymeric quaternary ammonium salt according to any one of Claims 1 to 10 as dyeing auxiliary.
33. Process according to claim 32, wherein the dyeing auxiliary is a levelling agent.
34. Process according to claim 32, wherein textile materials containing anionically modified polyester fibres are dyed in the presence of at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10.
35. Process for dyeing according to claim 32, wherein textile materials containing polyacrylonitrile fibres are dyed with cationic dyestuffs in the presence of at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10.
36. Process for rendering textile materials containing synthetic organic fibres antistatic, wherein the textile materials are treated with an aqueous or aqueous-organic solution or dispersion of at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10.
37. Process for fixing dyeings on textiles and paper wherein these dyed substrates are treated with at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10.
38. Process for providing substrates with an antimicrobial finish wherein these substrates are treated with at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10.
39. Process for purifying effluents, wherein a polymeric quaternary ammonium salt according to one of claims 1 to 10 is employed as a precipitant.
40. Process for coagulating colloidal aqueous dispersions, wherein a polymeric quaternary ammonium salt according to one of claims 1 to 10 is employed as a flocculating agent.
41. An aqueous or aqueous-organic solution or dispersion which contains a dyestuff and at least one polymeric quaternary ammonium salt according to any one of claims 1 to 10, for carrying out a process according to any one of claims 32 to 35.
42. Textile materials which contain natural or synthetic fibres and have been dyed or finished by a process according to any one of claims 32 to 37.
43. A compound of the formula shown in claim 1 substantially as described in any one of Examples 1 to 3.
44. A compound of the formula shown in claim 1 substantially as described in any one of Examples 4 to 15.
45. A process for the manufacture of polymeric quaternary ammonium salts substantially as described in any one of Examples 1 to 3.
46. A process for the manufacture of polymeric quaternary ammonium salts substantially as described in any one of Examples 4 to 15.
47. A process of use of a polymeric quaternary ammonium salt of the formula shown in claim 1, substantially as described in any one of Examples 16a, 17, 18, 19a, 20a and 21a.
48. A process of use of a polymeric quaternary ammonium salt of the formula shown in claim 1, substantially as described in any one of Examples 16b, 19b, 20b, 21b, 22 and 23.

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